

SCIENCE FOR CERAMIC PRODUCTION

UDC 666.762.2.93:666.3.056.5:669.27/28

METALLIZED COATINGS INDIFFERENT TO ALUMINUM NITRIDE CERAMICS

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Translated from Steklo i Keramika, No. 3, pp. 19–23, March, 1998.

A hypothesis is discussed the use of which can make it possible to achieve the maximum strength of metal-to-ceramic seals. The requirements of the conditions needed to obtain high-strength seals of aluminum nitride ceramics and metals chemically indifferent to it are postulated.

The development of metallized coatings for ceramic products is a labor-consuming process that is usually reduced to the selection of the optimum proportions of the coating components. In most cases the main criterion is the bond strength of the coating to the ceramic [1]. In the present work the strength of the metal-to-ceramic seal was determined by calculations based on binary systems with no noticeable chemical interaction.

The authors suggested that in order to achieve the highest strength of the metal-to-ceramic seal, a metallized coating should contain equal volumes of dielectric and metallic components. In this case to calculate the optimum mass ratio of the components, the following equations can be applied:

$$C_m = \frac{100}{1 + \frac{\rho_m}{\rho_d}};$$

$$C_d = \frac{100}{1 + \frac{\rho_d}{\rho_m}},$$

where C_m is the metal content; C_d is the dielectric content; ρ_m and ρ_d are the densities of the metal and the dielectric, respectively.

This hypothesis was tested on the compositions W–AlN, Mo–AlN, and Nb–WAl. The error in determining the optimum proportion was 2–5 wt.%. Moreover, these formulas did not allow assessment of the strength level of the seals and its correlation with the strength properties of the components of the coating.

In the present investigation, the conditions allowing achievement of the highest strength of the seals when the relationship between the components provides for equal strength of the coating adhesion to the ceramic and the metal (the full-strength condition) are refined.

Considering the structure of the metal-to-ceramic seal (Fig. 1), several boundaries can be distinguished.

The most dangerous sites under seal loading are the areas of contact between components with heterogeneous phases (boundaries 3 and 4). Usually the strength of the proper seal components is quite substantial relative to the strength of transitional sites. The strength of the boundaries between the metal component (metal-to-solder-to-nickel) is also high enough and approaches the strength of the contacting substances.

The most typical type of seal failure is breaking off along the coating-to-ceramic boundary ("naked" break) and the

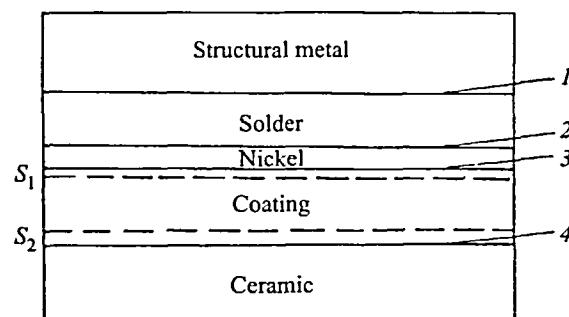


Fig. 1. Structure of the metal-to-ceramic seal. 1) structural metal-to-solder; 2) solder-to-nickel coating; 3) nickel coating-to-metallized coating; 4) metallized coating-to-ceramic; S_1 and S_2 are layers.

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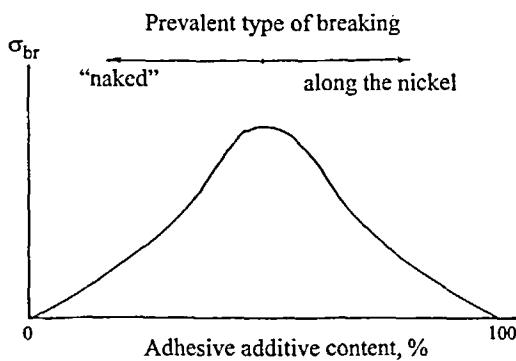


Fig. 2. Characteristic curve for a coating based on tungsten and molybdenum (addition of aluminum nitride, kaolin, glass).

nickel-to-coating (nickel break). The “naked” break is usually observed with a low content of the adhesive (dielectric) additive in the coating, and the nickel break occurs with a high content of adhesive additive. (Fig. 2)

It is obvious that the seal strength is limited by the strength of sites S_1 and S_2 (Fig. 1). In layer S_1 , “adhesive bridges” connect the nickel layer with the metallized layer via the metal particles of the coating, and in layer S_2 the strength of adhesion of the coating to the ceramic is contingent only on the particles of the dielectric phase. Thus, the adhesive strength of layer S_1 has to be determined by the strength of the metal matrix of the coating, and that of layer S_2 is determined by the strength of the dielectric matrix.

If interaction between the nickel and the dielectric phase particles of the coating is absent, then the dielectric phase particles in layer S_1 do not participate in forming adhesive bonds with the nickel layer and, consequently, their effect on the strength properties of site S_1 can be likened to the effect of pores.

Thus, using the Balshin equation (relationship between the strength and porosity of the material) [2], the strength of the contact between layer S_1 and the nickel can be represented as

$$\sigma_m = \sigma_{0m} (1 - V_m)^{n_m}$$

or assuming that $V_m = 1 - V_d$ we obtain

$$\sigma_m = \sigma_{0m} (V_d)^{n_m}, \quad (1)$$

where σ_{0m} is strength of the nonporous metal, MPa; V_d and V_m is the volume fraction of the dielectric phase and metal, respectively; n_m is an exponent related to the particle size ($n \approx 2 - 6$).

Accordingly, for layer S_2 the strength of the contact between the layer and the dielectric

$$\sigma_d = \sigma_{0d} (1 - V_d)^{n_d}, \quad (2)$$

where σ_{0d} is strength of the dielectric phase without pores; n_d is an index-related to the particle size.

All of these parameters are related to the particle size.

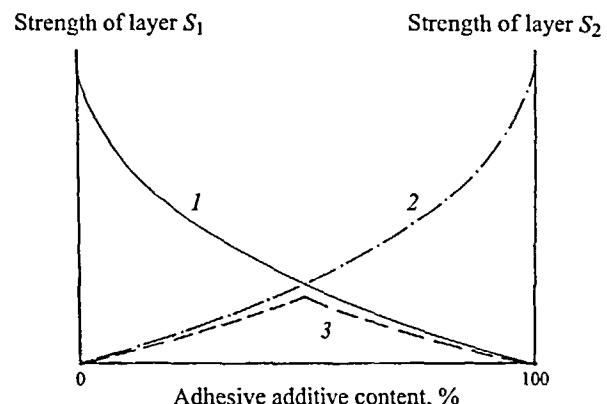


Fig. 3. Variation of the strength of layers S_1 (1) and S_2 (2) and overall strength (3) as a function of the phase content.

Since the coating is porous (and consists of three phases: metal, dielectric, and pores), Eqs. (1) and (2) take the following form:

$$\sigma_m = \sigma_{0m} (V_d - P)^{n_m};$$

$$\sigma_d = \sigma_{0d} (1 - V_d - P)^{n_d},$$

where P is the volume fraction of pores in the coating.

In this case the strength dependences of coating sites S_1 and S_2 have an intersecting point (Fig. 3) which characterizes the maximum level of the overall strength of the coating.

The resulting strength curve of the coating is described by the equation:

$$\sigma_s = \begin{cases} \sigma_m = \sigma_{0m} (V_d - P)^{n_m} & \text{at } \sigma_d \geq \sigma_m \\ \sigma_m = \sigma_{0d} (1 - V_d - P)^{n_d} & \text{at } \sigma_m \geq \sigma_d. \end{cases} \quad (3)$$

The solution of Eq. (3) makes it possible to know the strength properties of the components and to find their optimum proportion and the maximum strength of the coating.

The postulates considered were accepted as a working model of the seal strength.

It should be noted that this model cannot be applied to systems in which a chemical reaction occurs. Besides, this model does not account for the internal friction forces in the coating which can have affect the strength properties of the “matrix within matrix” type of system.

In the context of the fact that the published data on material strength mostly relate to samples containing pores, and the working model offers the strength value of nonporous materials (σ_{0m} and σ_{0d}) and power n related to the particle size, the investigation of the strength parameters of tungsten, molybdenum, and aluminum nitride was carried out.

Moreover, the strength of the samples is known to depend on their sizes [3, 4]. Therefore the use in the working

TABLE 1

Parameter	Sample material*					
	W _s	W _l	Mo _s	Mo _l	AlN _s	AlN _l
Molding pressure 50 MPa						
ρ _a , %	15.21	15.75	8.31	8.50	2.57	2.88
P _t , %	20.9	18.1	18.5	16.7	21.3	11.7
ρ _a /ρ	0.791	0.819	0.815	0.833	0.788	0.883
σ _{bend} , MPa	154	160	126	133	108	146
Molding pressure 75 MPa						
ρ _a , %	15.50	14.71	3.05	9.00	2.91	2.90
P _t , %	19.4	23.5	11.3	11.8	10.8	11.0
ρ _a /ρ	0.806	0.765	0.887	0.882	0.893	0.890
σ _{bend} , MPa	156	130	167	159	155	148
Molding pressure 100 MPa						
ρ _a , %	17.35	16.92	9.42	9.36	2.99	2.98
P _t , %	9.8	12.0	7.6	8.2	8.3	8.6
ρ _a /ρ	0.902	0.880	0.924	0.918	0.917	0.914
σ _{bend} , MPa	230	202	185	180	170	160
Molding pressure 100 MPa						
ρ _a , %	18.23	18.08	9.6	9.48	3.05	3.74
P _t , %	5.2	6.0	5.9	7.1	6.4	6.9
ρ _a /ρ	0.976	0.940	0.941	0.929	0.936	0.933
σ _{bend} , MPa	275	260	210	191	193	178
σ ₀ , MPa	325.3	315.2	250.1	240.0	229.2	224.7
n	3.293	3.350	3.372	3.246	3.202	3.553

* Index "s" is given to the samples of sizes 45 × 5 × 5 mm, index "l" to samples of 60 × 7 × 7 mm.

model of the values of σ_{0_m} and σ_{0_l} obtained on samples whose size exceeds by many times the coating size would be incorrect.

For the analysis and the calculation, it is necessary to take into account the relationship between the strength and the porosity, the geometric size, and the granular composition of the samples. Therefore, determination of the strength parameters normalized taking into account the scale factor was carried out according to the following procedure:

— manufacture of samples (rods) of different porosity (P₁ and P₂) and sizes (V₁ and V₂) and determination of their bending strength by the method of three-point loading;

TABLE 2

Material	Section, m ²	σ _{bend} , MPa	m	σ _{tc} , MPa	n
W	13.85	325.3	22.77	289.92	3.32
	28.4	315.2			
Mo	12.69	250.1	18.24	218.12	3.31
	27.0	239.96			
AlN	-17.54	229.2	24.8	207.5	3.38
	28.68	224.7			

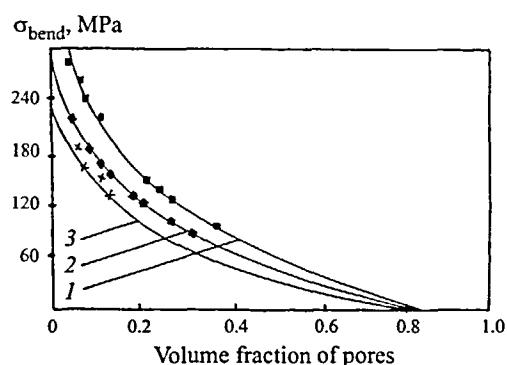


Fig. 4. Dependence of the sample bending strength σ_{bend} on the volume fraction V of the passive phase (porous). 1) Molybdenum, 2) tungsten; 3) aluminum nitride.

— determination of σ_{bend} and exponent n by approximation of the data obtained using the equation (σ₀ and σ_p are the strength of material without pores and with pores, respectively)

$$\sigma_{p_{bend}} = \sigma_{0_{bend}} \left(\frac{\rho_a}{\rho} \right)^n,$$

where ρ_a and ρ are the apparent density and true density, respectively;

— determination of the homogeneity coefficient of the materials studied and conversion of σ_{0_{bend}} taking into account the coating sizes σ_{0_{tc}} using the Weibull correlation

$$\frac{\sigma_1}{\sigma_2} = \left(\frac{V_2}{V_1} \right)^{-m}, \quad (4)$$

where σ₁, σ₂, and V₁ and V₂ are the strength and effective (undergoing loading) sample volume; m is the homogeneity coefficient;

— conversion of the bending strength of the coating σ_{0_{tc}} to the tensile strength of the coating σ_{0_{tc}} using the Weibull correlation

$$\frac{\sigma_{bend}}{\sigma_p} = [2(m+1)]^{-m}.$$

In order to obtain samples of different porosity, molding powder of the materials investigated was molded into rods of two sizes at a pressure ranging from the bottom limit of moldability up to 150 MPa. Firing was carried out under the same conditions in a SShV furnace in helium at the temperature of 1800°C. The duration of holding at the maximum temperature was 2 h. The average values of the strength and density are given in Table 1.

The data obtained were used to calculate σ₀ and exponents n of the materials studied.

TABLE 3

Paste	Content, %						σ_{br} , MPa		
	by volume			by mass			experimental data	calculated from the model	
	W	Mo	AlN	W	Mo	AlN		P = 5%	P = 10%
1	70	—	30	93.5	—	6.8	2 × 0.5	2.3	1.1
2	60	—	40	89.8	—	10.2	6 × 1	7.2	4.3
3	55	—	45	87.8	—	12.2	10 × 2	11.3	7.2
4	50	—	50	85.5	—	14.5	14 × 3	16.8	11.3
5	45	—	55	82.8	—	17.2	12 × 3	16.4	10.5
6	40	—	60	79.7	—	20.3	7 × 2	10.5	6.3
7	30	—	70	71.7	—	28.3	3 × 0.5	3.4	1.6
8	—	60	40	—	82.4	17.6	8 × 2	7.2	4.3
9	—	55	45	—	79.3	20.7	12 × 2	11.3	7.2
10	—	50	50	—	75.8	24.2	13 × 3	16.8	11.3
11	—	45	55	—	71.9	28.1	10 × 2	12.8	8.2
12	—	40	60	—	67.6	32.4	7 × 1	8.3	5.0

The estimated curves of the bending strength (Fig. 4, the points indicate experimental data) show that the sample strength depends significantly on its porosity. When the share of the passive phase (pores) in the material increases to 50%, its strength decreases by approximately ten times.

Since under three-point loading only a narrow segment of the rod (at the site of load application) experiences the maximum destructive loading, the relationship between the effective volumes in Eq. (4) were taken to be equal to the relationship between the effective sections of the samples.

In converting the strength of the sample to the tensile strength of the material in the coating σ_{tc} the value of 4 mm² was taken as the effective section of the seals under loading. This value is equivalent to the average section of the blade seal break used to determine the strength of the experimental coatings.

The homogeneity coefficients and strength parameters of the materials investigated as well as the initial values of the effective sections and bending strength σ_0 measured are given in Table 2.

In order to test the working model, metallized pastes based on tungsten and molybdenum with the aluminum nitride dielectric additive were prepared. The pastes were de-

posited on sintered ceramics and fired according to the firing procedure for AlN ceramics (burning-in temperature of 1800°C, holding time of 2 h).

The properties of the W-AlN and Mo-AlN pastes correlate best with the conditions accepted in the working model, that is to say: chemical interaction in the metal (W, Mo)-dielectric (AlN) system is absent; the strength of the coating at the boundary of the dielectric additive is determined by the strength of the material; W-AlN, and Mo-AlN systems are capable of sintering at a temperature of 1800°C to a relative density of 90–95% and even more (some known cermets of these compositions are used as adsorbents of UHF energy).

The compositions of the experimental pastes, the average values of the tensile strength σ_{br} obtained from the experimental data and model-based calculations are given in Table 3.

The average experimental values of σ_{br} agree well with the calculated density values. For W-AlN and Mo-AlN pastes (Fig. 5), all experimental values are found between the strength curves calculated for a coating with a porosity of 5 and 10%.

It is most likely that the coatings have porosity of 5–10% which can vary depending on the proportion of the components of the coating. Perhaps this explains certain deviations of the experimental data from the calculated strength curve.

It should be noted that the strength properties of the coatings depend on the proportion of the components by volume. The best results in strength were achieved in samples containing metal and adhesive components in a ratio by volume of approximately 1 : 1.

The initial data used for the calculation of the coating strength were the values of σ_{tc} and n (Table 4).

The model proposed agrees well with the experimental data. The analysis of this model reveals that the strength properties of the coating depend largely on its porosity. With

TABLE 4

P, %	Optimum content of W-AlN in the coating, %				σ_{br} , MPa	Optimum content of Mo-AlN in the coating, %				
	by volume		by mass			by volume		by mass		
	W	AlN	W	AlN		Mo	AlN	Mo	AlN	
0	47.1	52.9	84.0	16.0	28.29	49.1	50.9	75.1	24.9	25.26
5	47.4	52.6	84.2	15.8	19.94	49.2	50.8	75.1	24.9	17.79
10	47.7	52.3	84.3	15.7	13.49	49.3	50.7	75.1	24.9	11.95
15	48.0	52.0	84.4	15.6	8.66	49.4	50.6	75.4	24.6	7.63

porosity equal to 0 in the W-AlN coating, the estimated value of σ_{br} is 28.3 MPa, and with an increase in the porosity to 10%, the strength decreases by half (to 15.5 MPa). A similar correlation is observed in the Mn-AlN coating, but in that case the porosity has a weak effect on the optimum ratio of the components which remains practically constant with variation of the coating porosity between 0 and 15%.

In addition to the porosity, the strength properties of the components comprising the coating have a considerable effect on the coating strength. Thus, the strength of tungsten-containing coatings is somewhat higher than that of molybdenum-containing coatings. At the same time the following correlation is observed: the higher the relative strength of the component, the lower is its optimum content in the coating, and the greater is the share of the less strong component.

It is interesting to assess the maximum possible strength level of the metal-to-ceramic seal based on aluminum nitride. Thus, if in Eqs. (1) and (2) we set exponent $n = 2$ (according to the literature data such an exponent is typical for materials of amorphous and ultradisperse structures), the maximum possible average value of σ_{br} should be 60 MPa for the W-AlN coating with a content of the AlN additive equal to 16.7 wt.% (54.3 vol.%), and for Mo-AlN coatings it is 53.1 MPa for a content of AlN additive of 24.6 wt.% (50.6 vol.%).

The real values of σ_{br} of W-AlN pastes in the various experiments were 12–20 MPa (3–5 times lower than the maximum possible estimated value) and in Mo-AlN paste they were 10–15 MPa. This indicated that the data obtained referred to coatings of different densities and particle sizes.

Based on the above, the requirements for the conditions needed to obtain strong seals of AlN ceramics and metals chemically indifferent to AlN can be postulated.

The initial size of the coating particles, the burning-in temperature, and the holding time should be selected in order to produce a coating with the smallest possible size of the crystals and the highest possible relative density. At the same time, two mutually exclusive factors exist: on one hand, the coating density grows with an increase in the temperature and holding time, which causes a substantial increase in the seal strength, and on the other hand, the increase in the size of the crystals in the coating (high-temperature recrystallization typical of tungsten and molybdenum) significantly deteriorates the strength properties of the coating.

Thus, it is necessary to provide for the optimum size of the component particles in the initial coating, the optimum burn-in temperature, and the holding time. It is advisable to use additives which facilitate sintering of the coating or hamper crystal growth in the substances used as the main components of the coating.

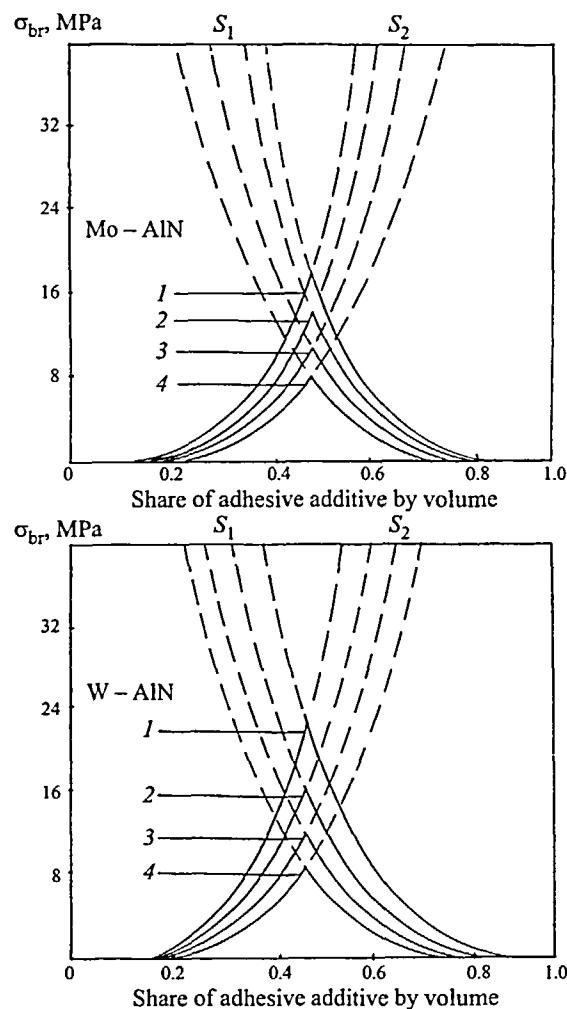


Fig. 5. Strength of coatings versus their composition. Continuous curves) strength of the coating; dotted curves) strength of layers S_1 and S_2 , respectively; 1, 2, 3, and 4) porosity of coatings 0, 5, 10, and 15%, respectively.

The optimum proportion of the paste components can be calculated using the model proposed.

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